Incorporation of Iron into Nickel-Based Phosphide as a Forward-Looking Electrocatalyst for the Oxygen Evolution Reaction in Metal-Air Batteries

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Motivation & Approach

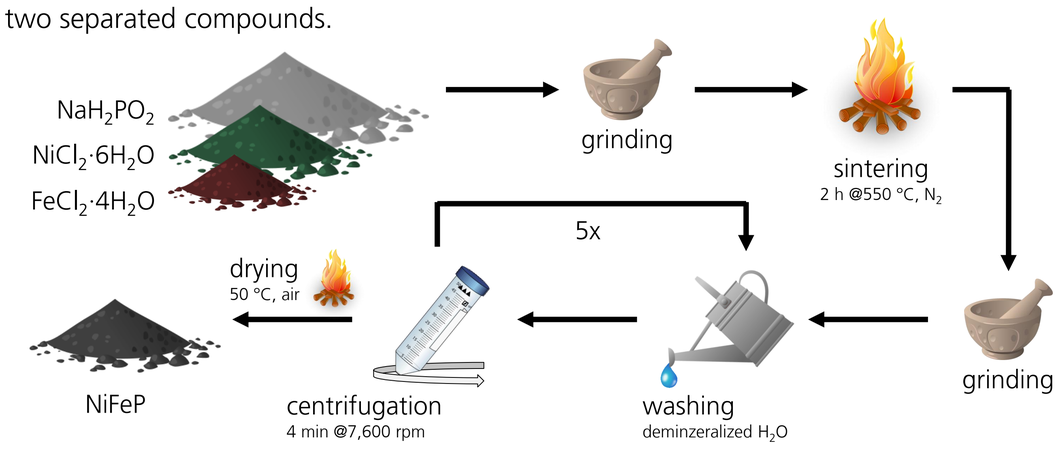
Electrolyzers as well as metal-air batteries are struggling with the slow kinetics of the oxygen evolution reaction (OER) during the charging process. Oxides of precious metals like iridium and ruthenium are commonly known for their exceptional ability to reduce the OER's overpotential in polymer electrolyte membrane electrolyzers. Unfortunately, these metals are very rare and thus expensive. To leverage a common use of metal-air batteries in future, OER catalysts based on low-cost materials like transition metals are in the focus of today's research.

Especially, nickel and iron are abundant and relatively inexpensive metals. Previous studies have demonstrated that double layered hydroxides containing both nickel and iron show higher activity than the same compounds containing only one transition metal. Iron is supposed to be the active site in such catalytic materials [1]. Hydroxides of nickel/iron are already well-known for their good performance in alkaline medium, whereas phosphides are just catching attention more and more.

Hence we aimed at synthesizing an OER catalyst for later application in metal-air batteries, combining the knowledge of nickel/iron catalysts and phosphide materials.

Synthesis

Starting from a simple and harmless synthesis route leading to nickel phosphide Ni_2P [2] we added an iron precursor to obtain a nickel-iron phosphide NiFeP with a molar ratio of 1.4:0.6:1.0. For this purpose, we adjusted the sintering temperature affecting the final composition and morphology. Sintering Ni and Fe precursors at 250 °C led previously to two separated compounds.



Methods of characterization

Electrochemical characterization:

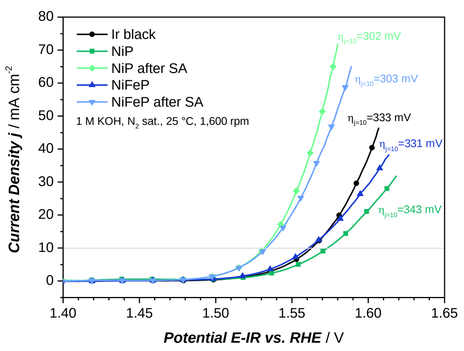
- Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) via rotating disk electrode (RDE)
  1. 10 to 1,600 mV·s^{-1} from 0.95 to 1.05 V // double layer capacity C_{dl}
  2. 3 cycles from 1.2 to 1.65 V; 5 mV·s^{-1} // OER activity
  3. 20 cycles from 0.3 to 1.5 V; 50 mV·s^{-1} // surface activation (SA)
  4. EIS @ 1.51 V from 50 mHz to 500 kHz // e.g. *IR* drop
  5. 3 cycles from 1.2 to 1.65 V; 5 mV·s^{-1} // OER activity
  6. 10 to 1,600 mV·s^{-1} from 0.95 to 1.05 V // C_{dl}

Additional physical characterization:

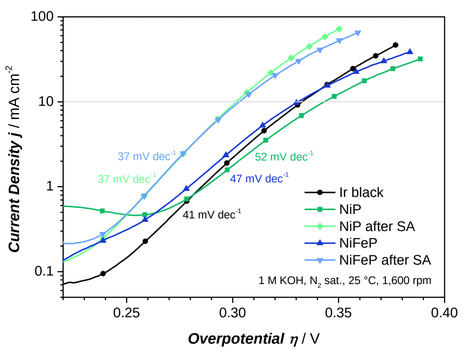
- Scanning electron microscopy (SEM)
- Energy dispersive X-ray spectroscopy (EDX)
- X-ray diffraction (XRD)
- X-ray photoelectron spectroscopy (XPS)

Results

CV:



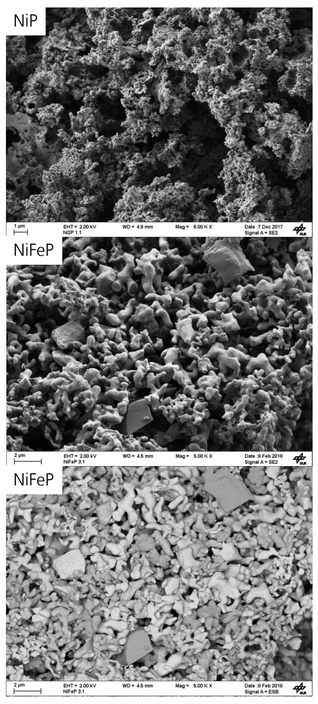
- The shown current densities *j* are capacity corrected; each measurement was performed with a catalyst loading of 0.06 mg·cm^{-2}
- NiP as well as NiFeP are much more active after surface activation due to oxidation of the outer shell [3], showing distinctly reduced Tafel slopes and an overpotential $\eta_{j=10}$ at 10 mA·cm^{-2}
- NiFeP after SA and NiP after SA clearly exceed the performance of state of the art OER catalyst Ir black



- C_{dl} of 63.7 µF·cm^{-2} (NiFeP), 80.0 µF·cm^{-2} (NiFeP a. SA), 66.6 µF·cm^{-2} (NiP), 83.4 µF·cm^{-2} (NiP a. SA) and 942 µF·cm^{-2} (Ir black) is calculated by plotting *j*/2 at 1.0 V over scan rate *v*

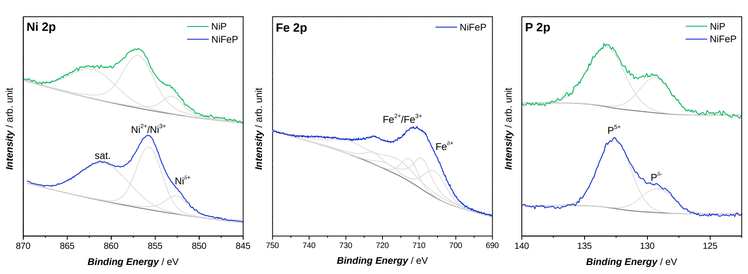
SEM/EDX:

- SEM unveils much coarser structure of NiFeP
- Relatively large and bulky particles with a high content of O (~45 m%) and P (~20 m%) are indicated by EDX
- A detector for backscattered electrons reveals two different shaded parts (see bottom fig.), small amounts of Fe (~10 m%) in darker parts
- Ni (70-80 m%) prevails in brighter parts, no significant Fe content



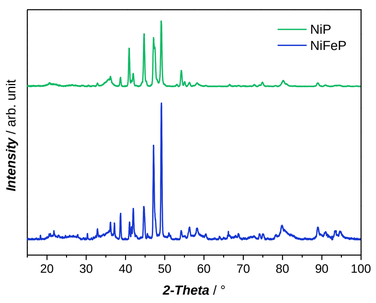
XPS:

- P 2p peaks indicate P^{5+} in phosphate (132.8 eV) and barely charged $P^{\delta-}$ in phosphide (129.2 eV) [4]
- The peak at 855.8 eV correspond to Ni^{2+}/Ni^{3+} and the one at 852.7 eV to $Ni^{\delta+}$ in Ni-P [4]
- Peaks at 709.6/713.0 eV and 723.2 eV may be considered as Fe^{3+} or even Fe^{2+}
- Fe-P can be recognized by $Fe^{\delta+}$ at 706.7 eV [4]



XRD:

- NiP consists of different nickel phosphides, predominantly Ni_2P and $Ni_{12}P_4$
- Most characteristic peaks of NiFeP between 39° and 54° are attributed to nickel phosphides, mainly Ni_2P and Ni_7P_3
- Some smaller peaks <39° and >62° can be indicative of FeP, but even iron phosphates, Fe_2O_3 and $FeCl_2$



Summary & Outlook

- Morphology of NiFeP is coarser than NiP due to the higher sintering temperature (550 °C vs. 250 °C)
- Physical characterization reveals a much lower amount of Fe than calculated
- Nevertheless, activated NiFeP shows very high OER activity compared to iridium black
- Since the conditions are obviously not ideal the synthesis route needs to be optimized leading to fine structures, full integration of iron and high purity without any phosphates and oxides

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European Commission | Horizon 2020 European Union funding for Research & Innovation

References:

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